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Freeze-Thaw Processes and Soil Chemistry

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Abstract

This review broadly examines the interactions between freeze–thaw processes and soil chemistry, focusing on 1) the effect of solutes on physical properties such as freezing-point depression, unfrozen water and frost heaving, 2) the effect of freeze–thaw cycles and low temperatures on soil chemistry, and 3) modeling of freeze–thaw processes and chemistry. The presence of solutes causes a freezing-point depression, which increases the amount of unfrozen water in soils. Liquid films on soil particles provide the dominant route for the flow of water and associated solutes in frozen soils. In general, salts reduce the hydraulic conductivity and water flow to the freezing front, which reduces frost heaving. Solute exclusion during freezing leads to supersaturated solutions, which promotes the precipitation of secondary minerals in soils. At the watershed level, ionic concentrations in early meltwaters are often 2–9 times higher than snowpack concentrations. Temperature is the dominant factor controlling decomposition rates, with minimal detectable rates occurring at temperatures as low as $-10°C$; both bacteria and fungi are physiologically active at subzero temperatures. Extracellular enzymes are active in soils at temperatures as low as $-20°C$; this activity is thought to occur in unfrozen water on surfaces of soil particles. Nitrogen mineralization is reported at temperatures as low as $1°C$ and is promoted by freeze–thaw cycles. There are strong and complex interactions among soil properties that control solute and water flows along concentration, temperature and hydrostatic gradients in freezing and frozen soils. These complex interactions *necessitate* the development of computer simulation models that can integrate physical–chemical properties and processes.

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Freeze–Thaw Processes and Soil Chemistry

GILES M. MARION

INTRODUCTION

This review will broadly examine the interactions between freeze–thaw processes and soil chemistry, relying primarily on the empirical record; the theoretical foundations for freezing and chemical interactions were discussed in another report (Grant, in prep.). In the first part of this report, I examine the effect of soil chemical properties on physical factors associated with freezing and thawing, such as freezing-point depression, unfrozen water content and frost heaving. The second part of this report will examine the effect of physical factors such as freeze–thaw processes and subzero temperatures on chemical reactions and chemical transport in soils. Then the effect of freeze–thaw processes and subzero temperatures on soil biology and soil remediation will be examined. And finally I will examine theoretical models for freezing and thawing processes that explicitly include chemistry.

EFFECTS OF CHEMISTRY ON SOIL FREEZING AND THAWING

Two important ways in which soil chemical properties influence soil physical properties in freezing and thawing environments are through freezing-point depression and unfrozen water content. These properties, in turn, affect water and solute movement in frozen soils, which influences soil strength, frost heaving and contaminant transport.

Soil moisture

Solutes lower the freezing point of water. The freezing-point depression in dilute solutions is given by the Van't Hoff equation (Lewis and Randall 1961):

$$dT/dm_B \approx -RT^2/(55.5\,\Delta H) \tag{1}$$

where m_B = molality of solute B (mol kg^{-1})
T = temperature (K)
R = gas constant (J K^{-1} mol^{-1})
ΔH = enthalpy of fusion of ice (J mol^{-1}).

This equation simplifies to:

$$\Delta T \approx -1.860\,(vm_B) \tag{2}$$

where ΔT is in °C and v is the number of aqueous species resulting from the dissolution of the solute (e.g., 1 for sucrose, 2 for NaCl, 3 for CaCl$_2$) (Lewis and Randall 1961). Therefore, the freezing point of a 0.1-mol kg^{-1} NaCl solution would be 0.37°C lower than the corresponding freezing point of pure water.

Equation 2 is general for "dilute" solutions and holds for all chemical species regardless of their degree of dissociation. However, departures from the limiting slope of -1.86°C/vm are apparent at concentrations $> 0.2\ vm$ (Fig. 1). These departures are most significant for electrolytes that dissociate into ions of higher valences (i.e., MgSO$_4$ > Na$_2$SO$_4$ > NaCl). Part of the explanation for the deviations from the limiting slope are attributable to ion pairing between oppositely charged species, which decreases the true concentration of chemical species in solution (e.g., one MgSO$_4^0$ ion pair instead of two separate Mg^{2+} and SO$_4^{2-}$ ions). In general, the strength of ion pairing is proportional to the product of the ionic charges (Davies 1962). Therefore, di-divalent ion pairs such as MgSO$_4^0$ are much stronger than uni-univalent ion pairs such as NaCl^0.

For a few salts, primarily highly soluble chlorides and sulfates, it is possible to construct complete phase diagrams at subzero temperatures. A
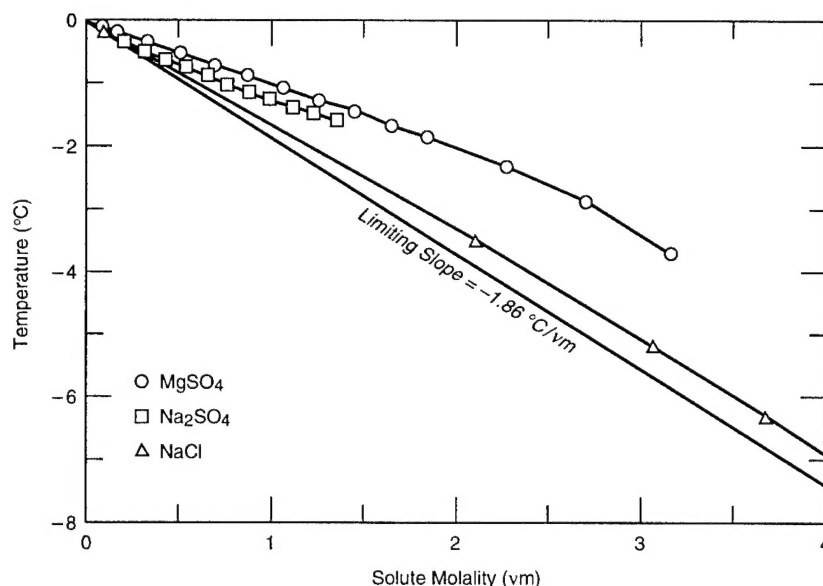
Figure 1. Freezing-point depression for three salt solutions. The data were taken from Linke (1965).

phase diagram for the H_2O–NaCl system at subzero temperatures (Fig. 2) is very useful in describing the change in the solution phase as ice and NaCl precipitate during the freezing process. Assume an initial NaCl concentration of 1.00 mol kg^{-1} and an initial temperature of 0°C. As this solution cools below 0°C, the NaCl concentration will remain constant until the temperature reaches –3.3°C, when ice, largely a pure phase, will begin to precipitate, concentrating NaCl in the remaining unfrozen solution. If equilibrium is maintained between the solution and ice phases during freez-

ing, then the NaCl concentration in solution will follow the ice–solution equilibrium line, increasing in concentration as temperature decreases until it reaches the eutectic composition at –21.2°C and 5.17 mol kg^{-1}, at which point the residual solution will solidify as a mixture of ice and $NaCl \cdot 2H_2O$.

The phase diagram (Fig. 2) can be used to estimate the unfrozen water content at any point in the freezing process. To facilitate these calculations, the following polynomial equations were fitted to the ice-solution and solution-$NaCl \cdot 2H_2O$ equilibrium data:
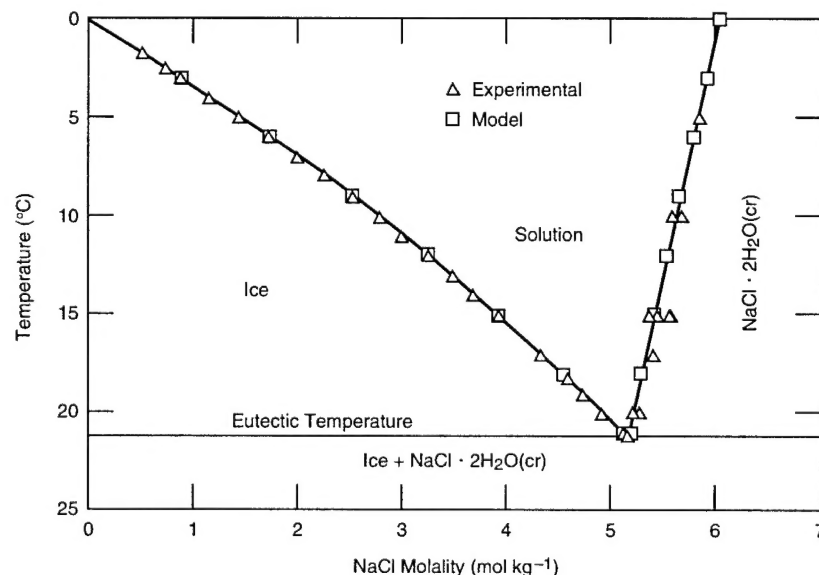
Figure 2. Stability diagram for the NaCl–H_2O system at subzero temperatures.

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$$\Delta T = -0.13 - 2.978\, m_{NaCl}$$

$$-0.211\, m_{NaCl}^2 \quad \text{(ice–solution)} \qquad (3)$$

$$R^2 = 1.000$$

$$\Delta T = -42.37 - 12.082\, m_{NaCl}$$

$$+\, 3.131\, m_{NaCl}^2\, \text{(solution–NaCl·2H}_2\text{O)} \qquad (4)$$

$$R^2 = 0.964$$

and

$$W_u = m_{Bi}/m_{Bf} \qquad (5)$$

where ΔT = freezing-point depression
m_{NaCl} = NaCl molality
W_u = fraction of unfrozen water
m_{Bi} and m_{Bf} = initial and final molalities.

Equation 5 assumes the precipitation of a pure ice phase. At $-10°$ and $-20°C$, the corresponding NaCl molalities are 2.77 and 4.94 mol kg^{-1}, respectively (eq 3). Therefore, the unfrozen water contents at $-10°$ and $-20°C$ for a solution that was initially 1.0 mol kg^{-1} are 0.361 (1.0/2.77) and 0.202 (1.00/4.94), respectively (eq 5). Conversely the frozen percentages are 63.9 and 79.8%. If the initial NaCl solution was 0.01 mol kg^{-1}, then the unfrozen fraction at $-20°C$ would be 0.00202 (0.01/4.94), with a frozen percentage of 99.8%. Clearly the concentration of salts in the solution phase during the freezing process, because of salt exclusion from the ice phase, can substantially alter the freezing point and unfrozen water contents of solutions.

The NaCl–H$_2$O phase diagram also demonstrates that an NaCl aqueous solution with an initial concentration <5.17 m will not precipitate NaCl·2H$_2$O until the temperature drops to $-21.2°C$ and the NaCl molality increases to 5.17 mol kg^{-1} (the eutectic point). On the other hand, if the initial NaCl molality is >5.17 mol kg^{-1}, then NaCl·2H$_2$O will be the initial phase to precipitate and ice will not form until the temperature drops to $-21.2°C$ and the NaCl concentration decreases to 5.17 mol kg^{-1}.

For soils the major factors influencing the freezing-point depression and unfrozen water contents are temperature, adherence of water to soil particles and solute concentrations (Hoekstra 1969, Anderson and Morgenstern 1973, Perfect et al. 1991, Frolov and Komarov 1993). The pure NaCl–H$_2$O phase diagram (Fig. 2) neglects soil solid–

water interactions and as a consequence only demonstrates qualitatively what might occur in a soil. For example, Frolov and Komarov (1993) demonstrated that NaCl solutions in soil remain unfrozen to temperatures lower ($-24°C$) than the eutectic for pure NaCl ($-21.2°C$, Fig. 2), presumably due to capillary effects.

Banin and Anderson (1974) examined solute effects on freezing-point depression by comparing the freezing points of soils, with and without NaCl additions. They found excellent agreement between experimental measurements and a theoretical solute model at low NaCl concentrations and a small but consistent underestimate (10–20%) of the experimental freezing point at higher NaCl concentrations. Suleimanov and Andronova (1990), using a similar theoretical solute model, reported a similar underestimate of the measured freezing point. Both studies suggested that this discrepancy was due to the inhomogeneous distribution of salt in water because of the negative adsorption of anions (anion repulsion) near negatively charged surfaces, which resulted in abnormally high salt concentrations in the bulk solution.

Yong et al. (1979) developed an unfrozen soil water model that explicitly accounts for negative salt adsorption using diffuse double-layer theory. This model showed excellent quantitative agreement with a montmorillonite soil sample but only qualitative agreement for kaolinite and grundite soils. This discrepancy was attributed to the model requirement for interlamellar migration of water in soil freezing, which is a reasonable assumption for montmorillonite but not for kaolinite or grundite. Yong et al. (1979) also pointed out examples where pure solution theory contradicts experimental measurements. For example, the unfrozen water content at subfreezing temperatures first decreases with the addition of salt to a minimum value around 10^{-3} mol L^{-1}, then increases with increasing salt concentration, as would be predicted from pure solution theory. There are strong interactions among soil surface area, charged surfaces, soil salts and moisture that control freezing-point depression and unfrozen water content of soils. A model that can describe these interactions quantitatively over a broad range of salt concentrations does not exist at present.

A number of papers have reviewed the physics of moisture movement in freezing and frozen soils (Hoekstra 1969, Anderson and Morgenstern 1973, Miller 1980, Perfect et al. 1991). This is a broad field, much studied and for the most part beyond the scope of this review. For the purposes of this re-

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view, I want specifically to examine the roles of soil chemical properties on moisture movement in freezing and frozen soils. Before discussing chemical effects, however, we need a theoretical framework for the discussion.

Following Perfect et al. (1991), we will use the nonequilibrium thermodynamic approach, where fluxes are written as explicit functions of both direct and coupled transport phenomena. For example,

$$j_w = -L_{wh}\nabla T / T - L_{ww}\nabla pl$$
$$- L_{ws}\nabla \pi - L_{we}\nabla \varepsilon \tag{6}$$

$$j_s = -L_{sh}\nabla T / T - L_{sw}\nabla pl$$
$$- L_{ss}\nabla \pi - L_{sc}\nabla \varepsilon \tag{7}$$

where

j_w and j_s = fluxes of liquid water and solute

∇T, ∇pl, $\nabla \pi$ and $\nabla \varepsilon$ = gradients in temperature, hydrostatic pressure, solute concentration and charge

L_{mn} = transport coefficient relating the mth flux (j_m) to the nth component.

Fluxes and their driving forces (gradients) in frozen porous media are summarized in Table 1.

Water moves in soil (j_w) in response to changes in the chemical potential of water, which is related to gradients in the hydrostatic pressure (∇pl) (Darcy's Law), temperature (thermo-osmosis), solute concentration (capillary osmosis) and electrical potential (electro-osmosis) (Table 1, eq 6).

At the freezing front in dilute solutions, anions (generally) are preferentially absorbed into the ice phase, leading to a measurable charge separation (freezing potentials); this phenomenon is called the Workman Reynolds Effect (Drost-Hansen 1967, Murphy 1970, Hanley and Rao 1982). Freezing potentials are properties of dilute solutions and pure water and disappear at high concentrations (Drost-Hansen 1967, Murphy 1970). Although Hanley and Rao (1982) developed a model to quantify the relation between freezing potentials and the migration of moisture and ions in freezing soil, the overall significance of this phenomenon for soil freezing is unclear. Another electrical phenomenon, electro-osmosis, can cause considerable water movement, but this is only important in cases where induced electrical potentials are applied to soils (Hoekstra and Chamberlain 1964). Outcalt et al. (1989) monitored electric potentials in freezing soils during diurnal and seasonal freeze–thaw cycles. They concluded that the rapid and systematic pattern of electrical potential variation during freeze–thaw events demonstrates that the effects of electrolyte concentration and dilution are products of evaporation–distillation, melting of frost-purified ice, soil water advection to the freezing region, electrolyte expulsion from the freezing region and infiltration of rain and snowmelt. They further concluded that soil electrical potentials will yield valuable information concerning the state and mobility of soil water in freezing and thawing soils.

In general, water moves from warm to cold, from regions of low solute concentration to high-solute regions and from high-moisture zones to low-moisture zones (Perfect et al. 1991). Chemical potentials of water due to gradients of hydrostatic pressure, solute concentration and temperature interact additively to create a strong thermodynamic sink for liquid water at the freezing front (Fig. 3). As soils freeze from the top downward, the thermal gradient will induce an upward flow of water to the freezing front. Solutes are largely excluded in the freezing process, and maximum solute concentrations are generally found imme-

Table 1. Matrix of direct and coupled transport phenomena in frozen porous media. (After Perfect et al. 1991).

	Driving force			
Flux	∇T	∇pl	$\nabla \pi$	$\nabla \varepsilon$
j_h	FOURIER'S LAW*	Thermofiltration	[Dufour Effect]†	Peltier Effect
j_w	Thermo-osmosis	DARCY'S LAW	Capillary osmosis	Electro-osmosis
j_s	Soret Effect	Reverse osmosis	FICK'S LAW	[Electrophoresis]
j_c	[Seebeck Effect]	Streaming potential	[Diffusion potential]	OHM'S LAW

* Direct processes are upper case; coupled processes are lower case.
† No reference to bracketed processes found in the soil freezing literature.
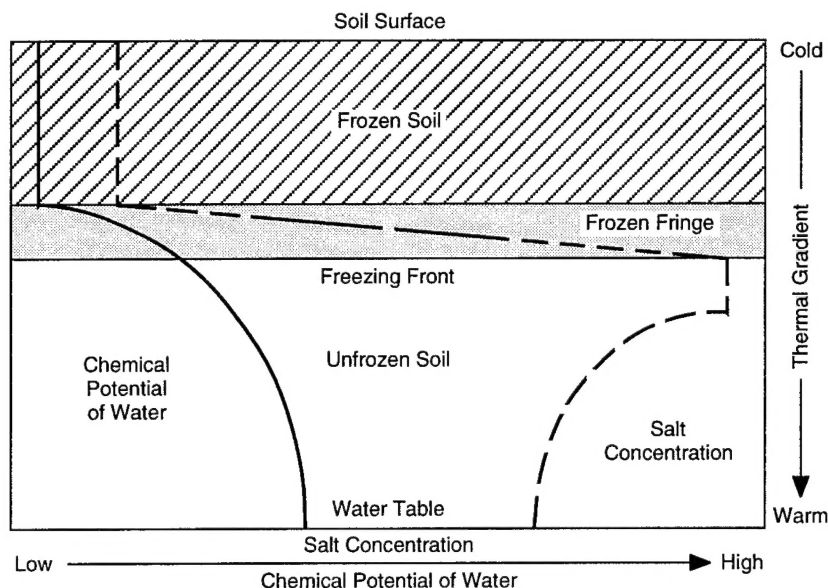
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Figure 3. Schematic of a freezing soil system.

diately in front of the freezing front (Hallet 1978, Miller 1980, Kay and Groenevelt 1983, Hofmann et al. 1990). This solute (or osmotic) gradient will generally induce an upward movement of water. And last, freezing of soil water, which is analogous to soil drying (Lahav and Anderson 1973, Miller 1980), creates a strong sink for water and induces an upward movement of water to the freezing front.

Under subzero temperatures some soil water remains unfrozen as thin films around soil particles and serves as an avenue for the movement of both water and solutes in frozen soil. From 0° to −1°C there is an exponential decrease in the hydraulic conductivity (L_{ww}, eq 6) of a frozen soil from 10^{-8} to 10^{-12}–10^{-14} m/s; below −1°C the hydraulic conductivity remains essentially constant (Perfect et al. 1991). Solutes can theoretically increase the water flux, in part because of the direct effect on water diffusion (L_{ws} in eq 6) but also because of indirect effects on freezing-point depression, unfrozen water content and increases in the thickness of soil moisture films (Anderson and Morgenstern 1973, Henry 1988). Despite these theoretical considerations, it appears that the dominant effect of solutes is generally a reduction in hydraulic conductivity (L_{ww}) that overwhelms the other terms in the water flux equation (eq 6). As a consequence, water flux to the freezing front is generally reduced by solutes (Kay and Scott 1973, Sheeran and Yong 1975, Chamberlain 1983, Cary 1987, Ershov et al. 1992).

Factors controlling the upward flux of water into the freezing and frozen soil zones are of critical importance in understanding practical problems associated with freezing and thawing phenomena such as soil strength and frost heaving.

Soil strength

Freezing, per se, invariably increases the mechanical strength of soils because of the strong bonding between ice and soil particles (Mahar et al. 1983). Freezing and thawing can either increase or decrease soil strength, depending on the degree of thaw weakening. With respect to clays, Chamberlain (1989) concluded that strength increases can be expected where there is an increase in consolidation and density during freezing and thawing; decreases in mechanical strength can be expected with highly cemented clays and clay soils that are highly overconsolidated before freezing. Rowell and Dillon (1972) found that clay aggregates were produced by freezing. After thawing, these aggregates swelled and dispersed, depending on electrolyte concentration, in a manner similar to aggregates formed by drying.

The presence of salts in soils generally decreases mechanical strength (Tyutyunov and Derbeneva 1970, Tsytovich et al. 1973, Mahar et al. 1982, 1983, Ogata et al. 1982, Chamberlain 1983). This decline in mechanical strength with increasing salt concentration is generally attributed to a lowering of the freezing point and, as a consequence, an increase in unfrozen water content. In addition to

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unfrozen water films around soil particles, larger unfrozen brine pockets can form during especially rapid ground freezing of saline soils, which also decreases the mechanical strength of soils (Mahar et al. 1982, Chamberlain 1983).

Kostetskaya (1977) found that NaCl brines freezing at the eutectic point (–21.2°C, 5.17 mol kg^{-1}; Fig. 2) are sludge ice and have zero strength. However, the addition of Na_2SO_4 to the NaCl brines or to gravel soils containing the same brines increased strength. Ogata et al. (1982) found that the compressive strength for sands, silts and clays generally decreased with increasing salinity. An exception to this generality occurred where soils were frozen at –32°C, where the compressive strength at 2 and 3% salinity was actually higher than at 1% salinity. They attributed this anomaly to the fact that –32°C was beyond the eutectic temperature of NaCl. Clearly complex interactions are possible among specific solutes, freezing and thawing, and soil physical properties.

Frost heaving

From the classical papers of Taber (1929, 1930) and Beskow (1935) to more recent reviews (Anderson and Morgenstern 1973, Sheeran and Yong 1975, Gilpin 1980, Miller 1980, Chamberlain 1981, O'Neill 1983, Derjaguin and Churaev 1986, Nakano 1990, Black and Hardenberg 1991, Perfect et al. 1991), frost heaving has been the subject of intense interest because of its importance for engineering in frost-susceptible environments. The stability of soils for road, railroad, airfield, building, underground storage and pipeline construction in cold regions are critically dependent on frost susceptibility.

Frost heaving is due primarily to the formation of segregated ice lenses in soil and only secondarily to volumetric expansion of water during freezing (Anderson and Morgenstern 1973, Mageau and Morgenstern 1980, Miller 1980, Chamberlain 1981). Three conditions must occur simultaneously for frost heaving to occur:

- A prolonged period of subfreezing temperatures;
- Frost-susceptible soils; and
- A source of water.

Several models have been proposed to explain frost heaving (Miller 1980, Chamberlain 1981, O'Neill 1983, Black and Miller 1985, Horiguchi 1987, Nakano 1990, Black and Hardenberg 1991), including:

- The capillary (or primary) heaving model;
- The secondary heaving model;
- The adsorption model; and
- The osmotic model.

Although these models differ in the details of the mechanisms responsible for frost heaving, there is general agreement on the factors influencing frost heaving (Miller 1980, Chamberlain 1981, O'Neill 1983, Perfect et al. 1991). These factors include:

- Soil texture (silts are more frost-susceptible than either sands or clays);
- Pore size (pore size controls capillary rise, soil suction and hydraulic conductivity, all of which are important in the movement of water to the freezing front);
- Rate of heat removal (there is a maximum rate of frost heave at intermediate rates of heat removal);
- Temperature gradient (this affects the thickness and hydraulic conductivity of the frozen fringe where ice lensing occurs) (Fig. 3);
- Moisture conditions (saturated soils with high water tables are most susceptible to frost heaving) and
- Overburden stress (the greater the overburden stress, the lower the frost heaving).

In general, salts reduce frost heaving (Beskow 1935, Kay and Scott 1973, Yong et al. 1973a,b, Sheeran and Yong 1975, Chamberlain 1983). Exceptions to this generality exists. For example, Beskow (1935) found that dilute NaCl solutions (≤ 0.05 M*) accelerated frost heaving, but more concentrated NaCl (0.1 M) as well as $CaCl_2$ (0.025–0.5 M) decreased frost heaving. Because of the generally ameliorative effect, solutes have been examined for their ability to reduce frost heaving. Lambe and Kaplar (1971) and Lambe et al. (1971) evaluated more than 50 additives classified under four functional groups (void fillers and cements, aggregants, waterproofers, and dispersants) for their ability to modify frost heaving. They found that a dispersant, tetrasodium pyrophosphate (TSPP), and an aggregant, ferric chloride, possessed good frost heave modifying capabilities. Both additives reduced frost susceptibility in soils from "medium to high" to "very low to low."

Sheeran and Yong (1975) have proposed five hypotheses to explain the effect of salts on frost heaving. Salts may affect:

- The position and temperature of the freezing front;
- The chemical condition of frozen soil;
- The permeability of frozen soil;

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* M is molarity (mol L^{-1}).

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- The rate of water movement to the freezing front; and
- The freezing process.

Salts are excluded in the freezing process, freezing points are depressed by salts, and unfrozen water contents are increased in the presence of salts. (See previous discussion on *Soil moisture*.) These factors would reduce the water available for forming segregated ice. Additionally, lower temperatures reduce the soil hydraulic conductivity (Perfect et al. 1991). Salts in freezing soils reduce the capillary rise and soil hydraulic conductivity (Kay and Scott 1973, Sheeran and Yong 1975, Chamberlain 1983, Cary 1987). These factors that reduce water flow to the freezing zone are probably the most significant factors explaining lower frost heaving in the presence of salts. The frozen fringe generally thickens in the presence of salts (Sheeran and Yong 1975, Yong and Sheeran 1978, Chamberlain 1983), which could reduce the water flux to segregated ice lenses.

Solutes clearly affect the lensing process (Sheeran and Yong 1975, Chamberlain 1983). Chamberlain (1983) found plentiful but thin ice lenses forming in the presence of salts. This type of ice lens formation could reduce the flow of water in the frozen fringe, where segregated ice forms. Salts can interact with soil particles, causing them to either aggregate or disperse, depending on solute type and concentration (Lambe et al. 1971, Sposito 1989); this, in turn, will affect soil permeability and the resultant water flux.

Salts may also affect the depth of frost penetration. The deeper the zone of freezing, the more important overburden pressure becomes in limiting segregated ice formation. Sheeran and Yong (1975) found that the depth to the freezing front decreased with increasing salt concentration. On the other hand, Mahar et al. (1983) found that the rate of advance of the freezing front increased with increasing salinity; they attributed this to the gradual release of the latent heat of fusion over a range of temperatures and depths due to changing solute concentrations. Cary (1987), using a simulation model, predicted a greater depth of frost penetration with increased salt concentration.

Contradictions abound in the literature on frost heaving, probably because of the complex interactions among the driving forces controlling this process. Frost heaving is clearly a complex process dependent on soil properties, moisture conditions, solute concentrations and energy balance. Such complexity can not be explained by simple models. Only a continuing effort to model this important phenomenon in all its complexity coupled with judiciously selected empirical lab and field studies, will ultimately lead to the ability to accurately predict frost heaving.

EFFECTS OF FREEZING AND THAWING ON SOIL CHEMICAL PROPERTIES

Freeze–thaw processes and low temperatures influence chemical reactions, chemical transport and nutrient availability in soils. These interactions, in turn, influence mineral weathering rates, pedogenesis, contaminant remediation and revegetation of disturbed lands in cold regions.

Chemical reactions

Two of the most important chemical reactions affected by freezing and thawing are precipitation–dissolution and cation exchange. Solute exclusion during ice formation leads to supersaturated solutions, which promotes the precipitation of secondary minerals in soil, alters solution-phase compositions (which may promote the dissolution of primary minerals) and shifts equilibrium toward increased mineral weathering (Fig. 4) (Hallet 1978, Zvereva 1982, Sletten 1988, Richardson et al. 1990). Martynenko et al. (1992) subjected ground primary minerals in oxalic acid solutions to 70 freezing cycles. The interaction of acidic hydrolysis and cryogenic comminution enhanced mineral grain fragmentation and chemical weathering.
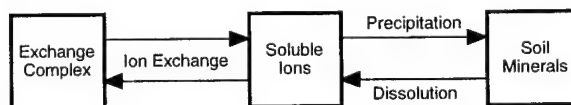
Figure 4. Ion exchange equilibria in a soil system.

The precipitation of silica in the lower horizons of soil profiles has been attributed to freezing (Slavnyy and Vorob'yeva 1962). The distribution of Na and Mg sulfate minerals in soils is temperature dependent, with low temperatures favoring the precipitation of Na sulfates (e.g., mirabilite: $Na_2SO_4 \cdot 10H_2O$) relative to Mg sulfates (Arndt and Richardson 1989, Richardson et al. 1990); in these papers it was hypothesized that freezing from the top down may concentrate the more soluble Mg sulfates at greater depth, leading to the development of surficial sodic (Na) horizons.

Freezing of Ca and Mg bicarbonate solutions leads to the precipitation of the more insoluble $CaCO_3$, thereby increasing the solution-phase Mg^{2+}/Ca^{2+} ratio (Vlasov and Pavlova 1969, Ivanov

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and Vlasov 1973, Sletten 1988). Sletten (1988) attributed the formation of aragonite, a relatively rare polymorph of $CaCO_3$ (Doner and Lynn 1977), to a more favorable Mg^{2+}/Ca^{2+} ratio in solution brought about by the differential solubilities of Ca and Mg carbonates. Hallet (1976) demonstrated that freezing strongly concentrates solutes in $CaCO_3$ solutions, which leads to the precipitation of $CaCO_3$. Based on temperature-dependent solubility data, Hallet estimated the eutectic temperature for pure $CaCO_3$ (–0.34°C). The relative insolubility of minerals such as $CaCO_3$ and $CaSO_4$ make them difficult to study at subzero temperatures because of the limited temperature range in which their single-salt solutions can co-exist in equilibrium with solid phase ice. This is in marked contrast to soluble chloride salts such as NaCl, which has a eutectic temperature of –21.2°C (Fig. 2), or $CaCl_2$, which has a eutectic temperature of –50.4°C (Spencer et al. 1990, Marion and Grant 1994).

Ion exchange reactions play a major role in controlling many physical and chemical properties of soils, such as aggregation, pH buffering and ion transport. Hinman (1970) found that alternate freezing and thawing increased exchangeable NH_4-N and decreased exchangeable K; there was no change in the cation exchange capacity (CEC) or exchangeable Ca and Mg. Pulubesova and Shirshova (1992) found no significant change in CEC or exchangeable Ca, Mg, K and Na in two soils and two clays (kaolinite and bentonite) following prolonged freezing (two months) and prolonged thawing (two months). Alternate cycles of freezing and thawing have led to both fixation of fertilizer K and release of crystal lattice K from K-depleted soils (Graham and Lopez 1969). Freezing increased adsorbed bases (the pH increased), while thawing increased soil acidity (the pH decreased) (Fedorov and Basistyi 1974). Deep freezing of soils with liquid N_2, which boils at –196°C, led to significant increases in the concentration of Ca, Mg and K in solution following thawing (Iskenderov 1976).

Surprisingly little work in soil science has examined the role of subzero temperatures on chemical thermodynamic equilibrium constants for cation exchange. Tyutyunova and Antipov-Karatatyev (1965) examined the Ca^{2+}-K^+ and the Mg^{2+}-K^+ exchange on montmorillonite, kaolin and soil over the temperature range from +20° to –17°C. Equilibrium constants at negative temperatures were determined in water–alcohol mixtures. There was an increased adsorption of K with decreasing temperature, which fell in the relative order:

kaolin > soil > montmorillonite. They reported standard Gibbs energies, enthalpies and entropies for ion exchange.

Chemical transport

When aqueous solutions freeze, solutes are largely excluded from ice. As a consequence, solute concentrations are generally highest at the freezing front (Fig. 3). Kay and Groenevelt (1983) derived a simple equation:

$$C_f = C_i + 80\,k\,C_i \qquad (8)$$

where C_i = original solute concentration
C_f = solute concentration at the frost front
k = solute inclusion coefficient.

If there is no solute inclusion in the frozen zone (k = 1), then the solute concentration at the freezing front could rise to 80 times the original concentration (assuming no salt precipitation). Such high concentrations can cause the freezing front to leap over solute pockets (Hallet 1978, Kay and Groenevelt 1983, Romanov and Levchenko 1989). These solute pockets may ultimately freeze, resulting in alternating bands of high and low concentrations in frozen soils (Romanov and Levchenko 1989). Kay and Groenevelt (1983) have argued that solute exclusion, which leads to narrow alternating high- and low-solute bands in soils, may not be a significant mechanism for macroscale solute redistribution in soils.

The dominant gradients that control the movement of solutes through freezing and frozen soils are concentration, temperature and hydrostatic pressure (Table 1, eq 7) (Cary and Mayland 1972, Baker and Osterkamp 1988, Qiu et al. 1988, Perfect et al. 1991). Solutes will diffuse from zones of high concentration (e.g., the freezing front) to zones of low concentration (Ficks Law, Table 1). In soils, solutes will move from warm to cold regions (Soret Effect, Table 1) (Cary and Mayland 1972, Qiu et al. 1988). However, the direct effect of temperature gradients on solute movement in soils is generally insignificant (Cary and Mayland 1972). Much more significant is the movement of solutes with water along hydrostatic gradients from warm zones to the freezing front (reverse osmosis, Table 1). Freezing of water creates a strong thermodynamic sink, and water will move in both the vapor and liquid (carrying solutes) phases to the freezing front (Cary and Mayland 1972, Gray and Granger 1986, Hofmann et al. 1990). In this process, solutes may move against a concentration gradient.

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The redistribution of solutes depends strongly on freezing rate, moisture content, soil texture and time. There are cases, especially in fine-textured soils, where maximum solute concentrations are found in the frozen zone (Ershov et al. 1992). Qiu et al. (1988) demonstrated that for single-salt solutions in moist sands, solutes migrate toward the unfrozen zone (Fig. 3); on the other hand, in silt and clay soils, solutes migrate toward the freezing zone. Over several freeze–thaw seasons, surficial salt applications may be leached to deeper soil horizons, effectively moving in the opposite direction of water during frost periods (Yong et al. 1973a). Baker and Osterkamp (1988) found that significant salt rejection and brine drainage occurred with downward freezing, but there was none with upward freezing. The amount of salt rejection increased with decreasing freezing rate. These differential responses are due to the role of soil physical properties such as porosity, surface area and hydraulic conductivity in controlling both water and solute flows along concentration, temperature and hydrostatic gradients. The complex interactions possible among soil physical and chemical properties is a strong incentive for developing computer simulation models.

Liquid films exist on soil particles in frozen soils, which provides the dominant route for the flow of water and associated solutes in frozen soils (Murrmann et al. 1968, Hoekstra 1969, Cary and Mayland 1972, Murrmann 1973, Gray and Granger 1986, Hofmann et al. 1990). Murrmann (1973) found surprisingly high diffusion rates for Na ions in the temperature range of 0° to –15°C, which he attributed to the existence of thin water films. Murrmann (1973) concluded that the temperature dependence of ionic diffusion at subzero temperatures is primarily a function of water film thickness. Even in Antarctic soils, which are continuously frozen and relatively dry, the liquid films at mineral surfaces are believed to be the dominant avenue for the movement of solutes (Ugolini and Anderson 1972, 1973).

Because many soil surfaces are charged and the solubility of different soil minerals are highly variable, ionic mobility depends on the specific ions. For example, Ugolini and Anderson (1972, 1973) found that Cl⁻ is more mobile in Antarctic soils than Na⁺, presumably because of the attraction between the negatively charged CEC and the positively charged Na ion. Czurda and Schababerle (1988) found that the monovalent cations Na and K were more mobile than the divalent cations Ca and Mg in frozen clay columns. This is probably because divalent cations have greater electrostatic attraction to charged surfaces than monovalent cations. More-soluble soil constituents migrate more readily through freezing and frozen soils because the less-soluble minerals precipitate; this can play a major role in horizonation and pedogenesis of cold regions soils (Hallet 1978, Zvereva 1982, Panin and Kazantsev 1986, Sletten 1988, Richardson et al. 1990).

The transport of solutes between water or snow and soil during freeze–thaw processes can play an important role in geochemical cycling in cold regions. Kadlec et al. (1988) found that the freezing of shallow waters in peatlands drives a considerable portion of solutes into the topsoil. Ostroumov et al. (1992) examined the flux of solutes from soil into snow under laboratory conditions. The maximum concentrations in snow were found at the snow–soil boundary. Solutes were transferred to snow in the same direction as the heat flux. The flux of ions in snow fell in the order: $K > Cl \gg Li > Ca > Cu \gg Cd = Pb$. They attributed the greater flux of K relative to Cl to greater anion adsorption, relative to cation adsorption, on the surface of ice particles. This charge separation phenomenon is identical to the Workman–Reynolds Effect, which is, however, usually thought to be due to absorption of anions into the ice phase.

Soil freeze–thaw processes can play a role in controlling geochemical cycling at larger scales, such as watersheds and geographic regions. Edwards et al. (1986) found that freeze–thaw cycles have significant effects on the chemical composition of streams. Substantial amounts of many elements that dominate stream chemistry become available upon thawing, especially Al, K and organic C. They also hypothesized that soil freezing might also influence solute chemistry by altering hydrologic pathways. Everett et al. (1989) concluded that snowmelt was the most important hydrologic and geochemical event in a small arctic watershed in northern Alaska. Ion concentrations were highest during the first 15% of the snowmelt event. In all cases ion concentrations in the spring runoff were four to nine times those of the snowpack. Potassium was present in surface waters only during meltoff and for a short time thereafter. Edwards et al. (1986) also reported the mobilization of K during the spring thaw. During winters with little or no snowmelt before spring, Johannessen and Henriksen (1978) found that 50–80% of the winter pollutant load is released with the first 30% of meltwater. Average solute concentrations were 2–2.5 times higher than snowpack concentrations.

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The resulting increases in acid concentrations of low-buffered waters occasionally lead to severe physiological stress on aquatic organisms. They hypothesized that these high concentrations may be due to a freeze-concentration process during snow recrystallization and melting in which solutes preferentially accumulate at surfaces of ice particles. Clearly snowmelt is a major hydrologic and geochemical event in regions subject to freeze–thaw cycles.

Ivanov and Vlasov (1973) concluded that cryogenic processes have the effect of forming waters that have low mineral concentrations and low Ca^{2+}/Mg^{2+} ratios in the Transbaikal region of Siberia. Factors that influence low mineralization are the freezing of soil solutions and groundwaters, the redistribution of salts between ice and liquid phases, the slow transition of salts into solution during thawing, and the precipitation of carbonates of alkaline-earth metals.

DECOMPOSITION AND NUTRIENT AVAILABILITY

How low temperatures and freeze–thaw cycles alter the soil as a medium for microbial activity and plant growth in cold regions soils is an important factor affecting revegetation, contaminant stability and carbon cycling. The availability of nutrients is critical for plant growth and, as a consequence, revegetation of severely disturbed lands. Organic contaminants can be directly decomposed by microbial activity, while mineral contaminants (e.g., Hg, Pb, Cd) can be absorbed by plants, reducing their mobility (Lagerwerff 1972, Page et al. 1987). Carbon fluxes from northern ecosystems may play a role in global carbon balance, affecting the global climate (Kvenvolden 1993, Marion and Oechel 1993, Oechel et al. 1993, Zimov et al. 1993).

Several chapters in a recent book edited by Chapin et al. (1992) discuss arctic ecosystems and microbial processes (Nadelhoffer et al. 1992), nitrogen fixation (Chapin and Bledsoe 1992) and plant nutrient absorption (Kielland and Chapin 1992). In the present review, our primary focus will be on the effect of low temperatures and freeze–thaw cycles on decomposition and mineralization processes. For fuller discussions of factors influencing microbial activity and plant growth in cold ecosystems, see the Chapin et al. (1992) book.

Temperature is the dominant factor controlling decomposition rates (CO_2 production), with minimal detectable rates occurring at $-10°$ to $-6°C$ (McCown et al. 1972, Flanagan 1978, Flanagan and

Bunnell 1980, Nadelhoffer et al. 1992, Gilichinsky 1992, 1993). Flanagan and Bunnell (1980) concluded that both bacteria and fungi are capable of growth at subzero temperatures. Decomposition rates increase with increasing temperature between $5°$ and $20–30°C$, and overall decomposition rates increase by 20% yr^{-1} for every 1000 degree-days above $0°C$ (Nadelhoffer et al. 1992).

It is well known that freeze–thaw cycles cause a respiratory burst of CO_2 and CH_4 following thawing (Mack 1963, Ivarson and Sowden 1970, McCown et al. 1972, Skogland et al. 1988, Christensen 1993). Skogland et al. (1988) attributed the respiratory burst to killing of bacteria, lysing of their cells and utilization of liberated carbon compounds as nutrients by the surviving bacteria. Ivarson and colleagues found strong correlations between extractable free amino acids and sugars (nutrients) and soil respiration, suggesting that microbial stimulation by nutrients was the cause of the CO_2 burst upon thawing (Ivarson and Gupta 1967, Ivarson and Sowden 1966, 1970). Ross (1972) found increased dehydrogenase activity with thawed soil samples in aerobic assays. He attributed this response to increased availability of substrates rather than multiplication of microorganisms because in anaerobic assays with shorter incubation times, the effects of increase substrate availability were less evident. McCown et al. (1972) attributed a spring CO_2 burst to trapping of CO_2 within the soil matrix upon bidirectional freezing, with subsequent release during spring warming; they believed this to be primarily a physical effect and not biologically mediated. In the latter study, soil surface temperatures beneath a snowpack were in the range of $-16°$ to $-10°C$; studies, previously cited, suggest that biological production of CO_2 does not become important until soil temperatures rise above $-10°C$. Christensen (1993) attributed the spring burst of CH_4 to the release of trapped CH_4 in the frozen soil and possibly also to changes in the production and consumption of CH_4 as temperatures increased and the active layer deepened.

The seasonal patterns of CO_2 and CH_4 emissions are important in assessing the role of these gases in the global carbon balance. Most of the evidence to date indicates that CH_4 emissions in the winter are insignificant in tundra soils (Whalen and Reeburgh 1992, Christensen 1993); however, evidence to the contrary also exists (Panikov and Zelenev 1992). Kelley et al. (1968) suggested that increased CO_2 concentrations at the soil surface beneath a snowpack at Barrow, Alaska, in the winter was due to microbial respiration as well as other physical

and chemical processes. Significant CO_2 emissions from wet tundra soils extended through February–March in some northern sites (Federov-Davydov 1993, Zimov et al. 1993). On the other hand, in other soils, CO_2 fluxes went to zero when soils froze (Federov-Davydov 1993, Zolotareva and Demkina 1993). Zimov et al. (1993) hypothesized that energy production by microbes was an important contributor to soil heat balance, preventing the freezing of the entire soil profile, which allows significant microbial activity to occur even during the winter. Because of the high temporal and spatial variability in winter gas fluxes (Federov-Davydov 1993, Zimov et al. 1993), their overall significance for the global carbon balance is unclear at present.

Extracellular enzyme activities (urease, phosphatase, sulfatase) have been detected in soils at temperatures as low as –20°C (Bremner and Zanuta 1975); these low-temperature activities are believed to be occurring in the unfrozen water at surfaces of soil particles. Freeze–thaw events in tundra water tracks in the fall can cause rapid decreases in soil redox potentials; associated with these changes are concomitant increases in extracellular enzyme activity (cellulases, phosphomonoesterase, proteases) (Linkins 1987). Enzyme activity continues to increase over three or four freeze–thaw cycles. It appears that the number of freeze–thaw events, rather than the duration of any one event, is the principal factor determining total enzyme activity. Linkins (1987) hypothesized that

higher plants may obtain a significant proportion of their annual nutrients during the fall as the result of increased soluble sugars, phosphorus and amino acids in solution.

The effect of freeze–thaw processes on nutrient availability is a critical factor in revegetation of severely disturbed lands in cold regions. Because nitrogen (N) is the element that most frequently limits terrestrial plant growth (Raven et al. 1986), it has been the most intensively studied nutrient in cold regions.

The dominant processes controlling the cycling of terrestrial N (Fig. 5) include:
- N_2 fixation, which directly converts atmospheric N_2 gas into organic N via N-fixing bacteria;
- Ammonification, which converts organic N into ammonium (NH_4^+);
- Nitrification, which converts NH_4^+ into nitrate (NO_3^-) through the nitrite (NO_2^-) intermediary;
- Cation-exchange reactions between NH_4^+ and exchange complexes;
- NH_4^+ fixation, which can render NH_4^+ difficultly exchangeable;
- Plant uptake of NH_4^+ and NO_3^-;
- Immobilization of NH_4^+ and NO_3^- by microbial processes;
- Denitrification, which converts NO_3^- into gaseous nitrogen (N_2) and nitrous oxide (N_2O);
- Ammonia (NH_3) volatilization, which converts NH_4^+ into NH_3 gas;
- Adsorption of NH_3 gas by soils; and
- Leaching, which is a particular problem for the negatively charged NO_3^- ion (Clark and Rosswall 1981, Marion 1987).

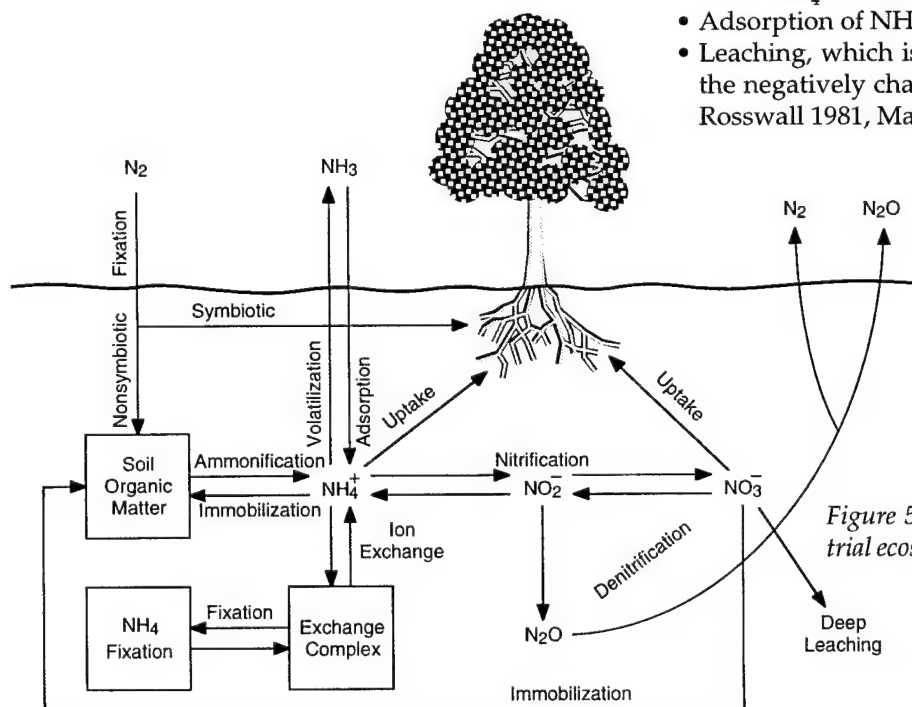Figure 5. Nitrogen cycle in a terrestrial ecosystem. (After Marion 1987.)

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Many of the reactions controlling nitrogen cycling (Fig. 5) are controlled by biological mechanisms. Examples include N_2 fixation (bacteria), ammonification (bacteria and fungi), nitrification (bacteria), denitrification (bacteria), immobilization (bacteria and fungi) and uptake (plants) (Clark and Rosswall 1981, Marion 1987). Some of the nitrogen cycling processes can also be accomplished by strictly abiotic mechanisms [e.g., ammonification via fire (Marion et al. 1991) and chemodenitrification (Christianson and Cho 1983)]. Nevertheless, it is clear that biological processes play a dominant role in controlling the flow of nitrogen as well as other nutrients through terrestrial ecosystems.

The responsiveness of nitrogen cycling processes at low temperature is critical to assessing the nitrogen supplying power of cold regions soils. Field measurements indicate net nitrogen mineralization at temperatures as low as 1°C (Gersper et al. 1980). Laboratory incubations have demonstrated that nitrogen mineralization (ammonification and nitrification) is less temperature sensitive at low temperatures (3-9°C) than at high temperatures (15-35°C) (Marion and Black 1987, Nadelhoffer et al. 1991, 1992). For example, at 35°C, nitrogen mineralization follows an exponential curve that shows a high initial rate of nitrogen mineralization followed by a gradually declining rate with time (Fig. 6); on the other hand, at 5°, 15° and 25°C, nitrogen mineralization follows a parabolic curve that shows a low initial rate of nitrogen mineralization followed by a gradual increase with time. The expo-nential mineralization curve is typical of temperate soils (Stanford and Smith 1972, Marion et al. 1981) but atypical of tundra soils in the temperature ranges normally encountered in cold regions. The slow release of nitrogen at low temperatures (Fig. 6) may be due to the generally unfavorable C/N ratios of the organic soils, which in one study ranged from 18 to 82 (mean = 40) (Marion and Black 1987). Flanagan and Bunnell (1980) reported a similar response for decomposers (CO_2 production) that responded more linearly at low temperatures and more exponentially at high temperatures.

Freeze–thaw cycles generally promote mineralization (ammonification and nitrification) of organic nitrogen, which leads to increased concentrations of NH_4^+ and NO_3^- (Soulides and Allison 1961, Mack 1963, Hinman 1970, Honnolainen and Reppo 1975, Malhi and Nyborg 1979, 1986, Gersper et al. 1980). An exception to this generality was reported by Read and Cameron (1979), who monitored mineral nitrogen forms in several soil types over 10 years. Between fall and spring, they found some increase in NO_3-N but a larger decrease in NH_4-N, resulting in a net decrease in mineral nitrogen during the winter. Malhi and Nyborg (1986) found large increases in mineral N when soils froze in the winter and large decreases in early spring when soils thawed; they attributed the spring loss to denitrification and not to leaching of NO_3^-. Christianson and Cho (1983) found that the maximum production of N_2 gas via chemodenitrification occurred at –3.5°C over the temperature range from –20° to
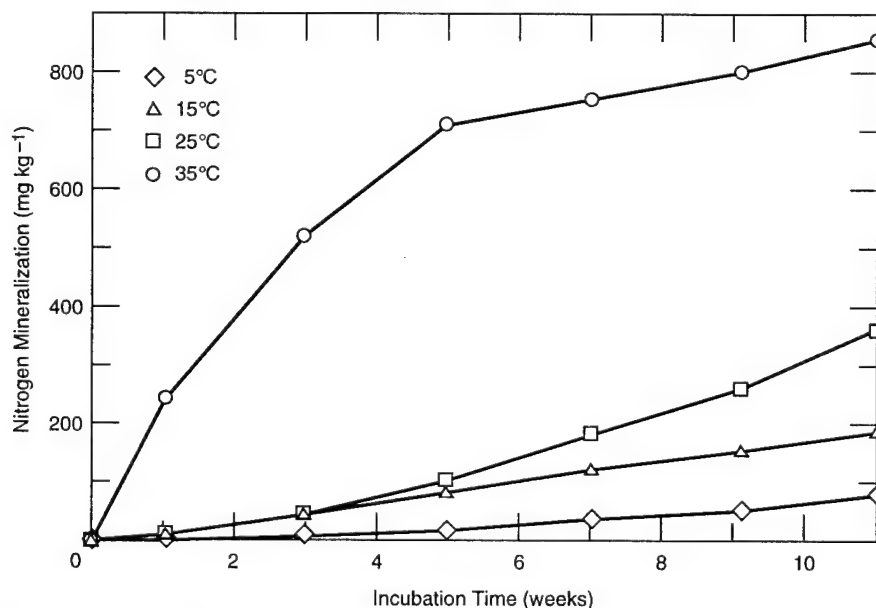

Figure 6. Cumulative nitrogen mineralization with time and temperature for an organic tundra soil. (After Marion and Black 1987.)

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+20°C; they attributed this freezing effect to the concentration of NO_2^- into the unfrozen soil water. Goodroad and Keeney (1984) found that N_2O concentrations and fluxes during the spring thaw were some of the highest values observed during the entire season. They attributed these high N_2O fluxes to the physical release of N_2O upon thawing and to production by denitrification. Edwards and Killham (1986) found that rates of both denitrification and NH_3 volatilization were increased by freeze–thaw cycles, especially in the presence of soils previously fertilized with urea (NH_2CONH_2). Campbell et al. (1970) found large and sudden unexplained decreases in exchangeable ammonium during the winter months following a steady fall buildup. Although they were unable to explain this phenomenon, possible explanations include enhanced denitrification, NH_3 volatilization and NH_4 fixation. These few papers indicate that freeze–thaw cycles affect mineral nitrogen forms, which are the forms utilizable by plants and also the forms that are most easily subject to gaseous losses (Fig. 5).

Hinman (1970) found that freeze–thaw cycles significantly increased the availability of extractable P in soils. On the other hand, Read and Cameron (1979) reported little change in the extractable P of soils from fall to spring over a ten-year period.

Exchangeable K, Ca and Mg typically either decrease in concentration or are unaffected by freeze–thaw cycles (Hinman 1970, Cheng et al. 1971). A decrease in exchangeable cation concentrations could be caused by the precipitation of soil minerals, which is promoted by soil freezing, causing a shift in the equilibria (Fig. 4).

Potassium and NH_4 are special cases among exchangeable ions because both are subject to fixation reactions (Fig. 5). Fixation is caused by the collapse of layer-lattice clay minerals, which renders ions in the interlayers slowly exchangeable. Fine et al. (1940) reported net releases of K subjected to freeze–thaw cycles in 75% of examined soils and a fixation in the remaining 25% of soils. Fine et al. (1940) also found that most clay minerals (bentonite, nontronite, Putnam clay, montmorillonite) released nonexchangeable K when subjected to freeze–thaw cycles. An exception was illite, a nonexpanding layer-lattice clay mineral, which fixed K. Graham and Lopez (1969) found that severely K-depleted soils will release K from fixed positions when subjected to freeze–thaw cycles. On the other hand, when K was added to soils, repeated freezing and thawing led to K fixation.

Manganese and Fe are also special cases among exchangeable ions because these ions may be present in both oxidized (Mn^{4+}, Mn^{3+}, Fe^{3+}) and reduced (Mn^{2+}, Fe^{2+}) forms, with reduced forms being more soluble in soils (Lindsay 1979). In general, soil moisture saturation promotes reduced forms and soil unsaturation promotes oxidized forms. Cheng et al. (1971) found that increasing soil moisture increased the availability of Mn and Fe. Under water-saturated conditions, repeated freeze–thaw cycles increased exchangeable Mn and Fe, while repeated freeze–thaw cycles in unsaturated soils decreased exchangeable Mn and Fe. The result for unsaturated conditions agrees with the general tendency for exchangeable K, Ca and Mg previously cited. The increased Mn and Fe concentrations under saturated conditions suggests that freeze–thaw processes may promote reducing conditions in soil, perhaps by excluding O_2 gas in the freezing process or because of slow diffusion of O_2 in frozen soils. This hypothesis might also explain the previously cited increased denitrification under freezing conditions (Christianson and Cho 1983, Edwards and Killham 1986) and the increased enzymatic activity under reduced conditions (Linkins 1987). Little work has been done on the effect of freezing and thawing on respiratory gas (O_2 and CO_2) balance in soils. This is a critical factor in controlling both plant and microbial activity in cold regions soils, with potential significance in understanding the global carbon balance.

SITE REMEDIATION

There are a number of cases where chemical composition and freeze–thaw processes interact, affecting the remediation of problem soils. These problem soils include saline soils, contaminated soils and frost-susceptible soils. The effect of soil salts in reducing frost susceptibility was discussed previously. Here, our focus will be on natural and artificial ground freezing as means for desalinating and decontaminating soils.

Kizilova (1959) examined the mobility and solubility of Na^+ and SO_4^{2-} ions under winter, but generally unfrozen, leaching conditions. The objective of winter leaching was to remove Na_2SO_4 from the soil profile; concern existed that $Na_2SO_4 \cdot 10H_2O$ (mirabilite) might precipitate at low temperatures. However, mirabilite did not precipitate even at subfreezing temperatures, and winter leaching was effective in removing Na^+ and SO_4^{2-} ions from these saline soils. Cary and Mayland (1972) examined a similar, but hypothetical, case. They pointed out that the lower solubility of $CaSO_4$ and $MgSO_4$ relative to Na_2SO_4 could cause the former

minerals to precipitate more readily upon freezing, causing an unfavorable $Na/(Ca+Mg)$ ratio in the solution, which could result in the dispersion of clay minerals and a sharp decrease in infiltration, problems generally associated with Na-dominated soils. Actually, at $0°C$, epsomite $(MgSO_4·7H_2O)$ is four times as soluble as mirabilite (Richardson et al. 1990). At freezing temperatures, $CaSO_4·2H_2O$ (gypsum) should first precipitate from solution during freeze-concentration of equal molal solutions, followed by mirabilite and finally epsomite. De Jong (1981) examined the freeze-purification of saline groundwater as a source of water for reclaiming saline soils. The initial 30% of the meltwater had a higher salt content than the original solution, and the last 70% had a lower salt content. The results suggest that freeze-purification of saline waters could be used in reclaiming saline soils by:

- Collecting and disposing of the initial meltwater and leaching with the later meltwater; or
- Using all the meltwater, which is a procedure similar to the high-salt-water dilution method of reclaiming saline soils (De Jong 1981).

Freeze–thaw processes may have both adverse and beneficial effects on contaminant transport through soils (Iskandar and Jenkins 1985, Iskandar 1986, Henry 1988). Adverse effects include frost heaving and reductions in the durability of clay liners, both of which can cause increased leakage from hazardous waste landfills. Additionally, freezing causes solute exclusion, which pushes contaminants out of soils, potentially contaminating groundwaters. Ways in which freezing can be used for beneficial uses include dewatering hazardous materials, building ice walls to contain contaminants, freezing of entire soil blocks to immobilize contaminants and freezing to push contaminants out of soils. Whether solute exclusion of contaminants is a beneficial or adverse effect of freezing depends on the control of the unfrozen effluent.

Since solute exclusion has been suggested as a possible mechanism for decontaminating soils (Iskandar and Jenkins 1985, Iskandar 1986, Ayorinde et al. 1988), factors controlling the process are critical for evaluating practical applications. A critical factor controlling the exclusion of solutes from ice is the rate of freezing. Romanov and Levchenko (1989) noted a marked increase in the effectiveness of exclusion with a decrease in the cooling rate from 0.5 to $0.25°C/day$. These workers also found that the effectiveness of solute exclusion increased with increasing solute concentration. In addition, the effectiveness of solute exclusion was much less in a

sand than in pure solutions. Baker and Osterkamp (1988) also found that the amount of salt rejection from the freezing region increased with decreasing freezing rate. Solute pockets that initially form in soils during freezing may ultimately freeze, resulting in alternating bands of high and low salt concentrations (Romanov and Levchenko 1989). On the other hand, Baker and Osterkamp (1988) found no evidence for salt banding in their freezing experiments. Solute exclusion that leads to alternating bands of high and low salt concentrations may not be a significant mechanism for macroscale solute redistribution in soils (Kay and Groenevelt 1983). A more thorough discussion on solute exclusion is given in the section on *Chemical transport*.

Iskandar and Jenkins (1985) examined the potential use of artificial ground freezing for contaminant immobilization. Frozen metal-contaminated soils eliminated metal leaching to groundwater. Freezing the soil from the bottom apparently enhanced upward movement of volatile organics to the soil surfaces, where losses occurred by volatilization. The amount lost depended on the mobility of specific organics and ranged from 90% for chloroform, benzene and toluene to as low as 45% for tetrachloroethylene.

Ayorinde and Perry (1990) examined the utility of freezing to move explosive compounds through soils. For one freeze cycle, they found a 40% reduction in concentration for meta-nitrotoluene (M-NT) and orthonitrotoluene (O-NT) and less than a 20% reduction for 2,6-dinitrotoluene (2,6-DNT) in frozen soil layers compared to unfrozen controls. At an average freeze rate of 0.4 cm day^{-1}, statistically significant movement was observed for M-NT and O-NT but not for 2,6-DNT. They postulated that for a given freeze rate, number of freeze–thaw cycles, type of soil and level of soil moisture, the ability to move contaminants through soils by freezing strongly depends on the type of contaminant, the initial concentration level and soil–contaminant interactions.

In another laboratory study, Ayorinde et al. (1988) showed significant mobility of volatile organics, such as benzene, chloroform and toluene, through a Lebanon silty soil frozen from the bottom up. They found a 25–67% reduction in contaminant concentration in the frozen soil but no corresponding increase above the freezing front. They attributed this discrepancy to contaminant losses through volatilization, biodegradation and sorption.

MODELING

Solutes in saline environments play a critical role in defining freezing and thawing of these systems. A few mathematical models have been developed that explicitly consider the effect of solutes on freeze–thaw processes. These models can be divided into three classes:
- Chemical thermodynamic equilibrium;
- Solute segregation at the water–ice interface; and
- Solute segregation in soil systems.

Classical chemical thermodynamic models only provide information on the states of systems at equilibrium; they do not describe the pathways to the equilibrium states. Their utility depends on how well natural systems that are constantly fluctuating can be approximated by the equilibrium states. Spencer et al. (1990) developed a chemical thermodynamic model (Spencer–Møller–Weare model) valid over the temperature range of –60° to +25°C, for the system Na-K-Ca-Mg-Cl-SO$_4$-H$_2$O. This model is parameterized with data from pure binary and ternary salt solutions. This model predicts the formation of ice and the precipitation of 15 chloride and sulfate salts, which allows the accurate prediction of the freezing point and chemical composition of simple and complex solutions, including seawater. Marion and Grant (1994) have developed a Fortran version of the Spencer–Møller–Weare model called FREZCHEM. The FREZCHEM model has two reaction pathways:
- Freezing at variable temperature and fixed water; and
- Evaporation at variable water and fixed temperature.

These two models can accurately estimate the chemical composition (Fig. 7) and unfrozen water (Fig. 8) of seawater at least down to –30°C. At lower temperatures some discrepancies exist [e.g., Mg concentrations (Fig. 7) and unfrozen water (Fig. 8)]. Given the difficulties in making experimental measurements at low temperatures, it is impossible with the presently available data to determine whether the model or the experimental measurements are most accurate at low temperatures (Marion and Grant 1994). Note that even at temperatures as low as –50°C, a small fraction of seawater (0.3%) remains unfrozen. The importance of salt precipitation during the freezing process is demonstrated for Na and Cl salts (Fig. 9), where only 0.3% of Na and 4.5% of Cl remain in the solution phase at –50°C.

These papers make it clear that to accurately interpret or model solute effects during freezing and thawing of saline solutions such as seawater, we need accurate chemical thermodynamic data on mineral solubilities at subzero temperatures. Apparently the databases for handling chloride salts down to the eutectic temperature of seawater (–54°C) are adequate (Spencer et al. 1990, Marion and Grant 1994). However, there are problems in modeling some sulfate salts at subzero temperatures, which may be due to poor-quality solubility data, to lack of data for some salts such as CaSO$_4$ and perhaps to an inadequate solution-phase model for concentrated sulfate solutions (Bukshtein et al. 1953, Linke 1965, Spencer et al. 1990, Marion and Grant 1994). The quantity and quality of data for the bicarbonate and carbonate salts of Na, K, Ca and Mg at subzero temperatures are even more sparse (Bukshtein et al. 1953). More research is clear-
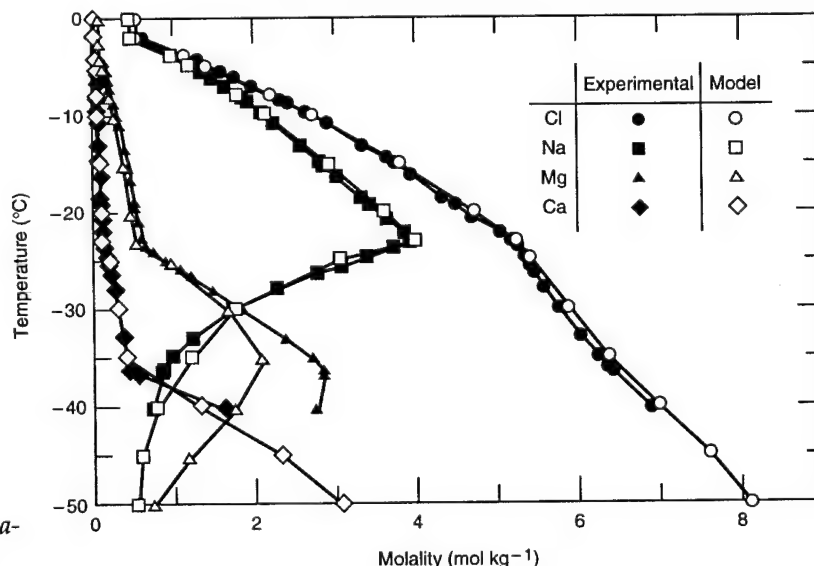

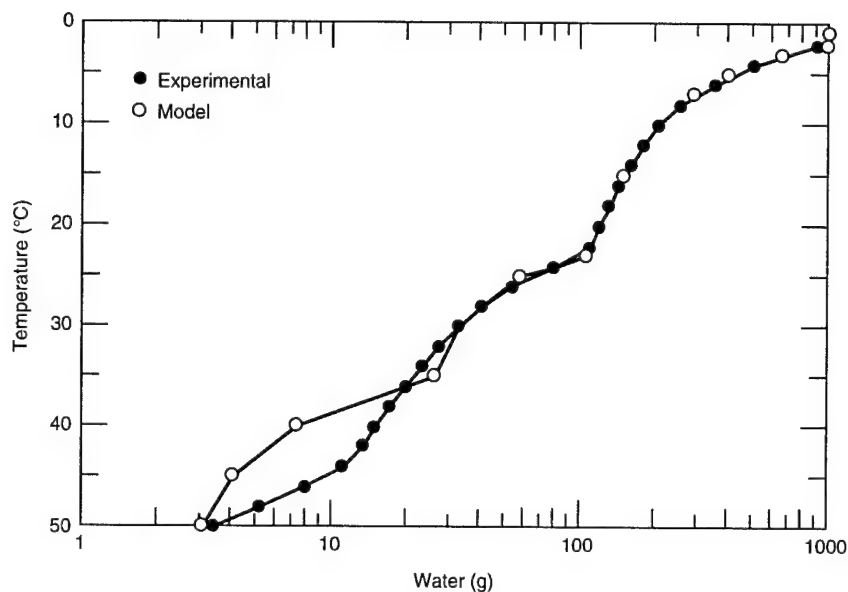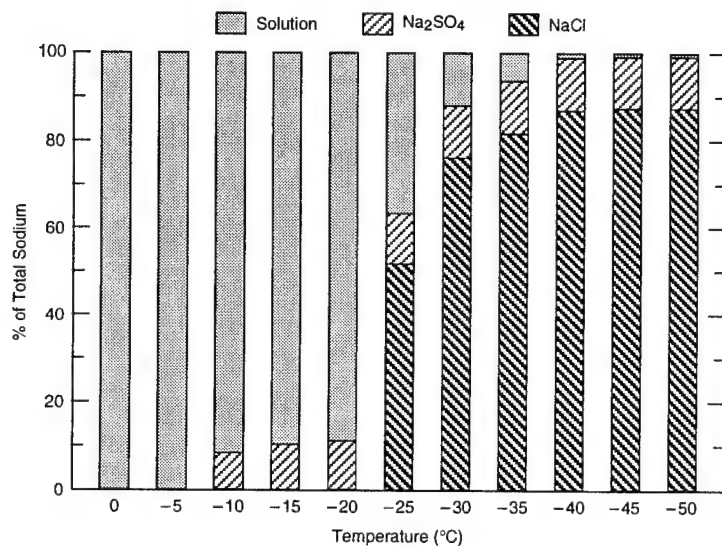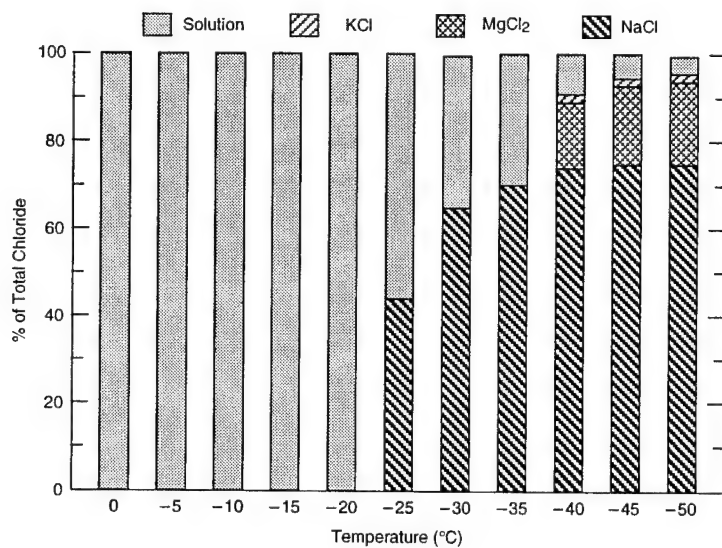Figure 7. Concentrations of major seawater constituents during freezing.

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Figure 8. Unfrozen water during seawater freezing.

a. Sodium.

Figure 9. Distribution of sodium and chloride during seawater freezing.

b. Chloride.

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ly needed to accurately assess the solubilities of the sulfate, bicarbonate and carbonate salts of Ca, Mg, K and Na at subzero temperatures before these constituents can be accurately integrated into geochemical models and ultimately into soil physical–chemical models.

Leung and Carmichael (1984) developed a model to describe solute partitioning between water and ice during freezing. This model can be used to estimate partition coefficients from experimental data. Working with slurries, Hanley and Rao (1982) developed a model based on freezing potentials that takes into account the diffusion of cations in the unfrozen portion of the sample, the separation of ions at the freezing front, and the migration of moisture and ions towards the freezing front.

Several models have been developed that describe the dynamics of freeze–thaw processes and solute redistribution in soils. Mahar et al. (1983) incorporated solute effects into a variation of the "Guymon" model to describe freezing of saline soils. They demonstrated that analytical modeling of freezing front penetration underpredicts the rate of freezing when no account is made for the effects of salinity. They also found that the rate of advance to a given depth of freezing increased with increasing salinity; they attributed this to the gradual release of the latent heat of fusion over a range of temperatures and depths due to changing solute concentrations. Osterkamp (1987) developed an analytical solution for freezing and thawing of soils containing water or brines. This model used empirical data on seawater brine concentration as a function of temperature to parameterize the model. Osterkamp (1987) found that maximum ice penetration is greater in the present of brines, which is similar to findings of Mahar et al. (1983).

Kadlec et al. (1988) developed a mathematical model to describe the solute segregation process at the freezing front and solute transport in the unfrozen water of peatlands. This model demonstrated the downward movement of solutes, which is important for establishing the geochronology of deposits and determining the nature of pollutant burial. Cary (1987) developed a numerical model for calculating frost heave that couples flows of heat, water and solutes as unsaturated soils freeze. This model demonstrated, as noted previously under *Frost heaving*, that increasing solutes can decrease frost heaving by reducing water flows to ice lenses. To my knowledge, this is the only frost heaving model that explicitly includes solute effects.

As this review has shown, many factors with complex interactions contribute to the differential movement of water and solutes in freezing soils. Because of the complexity of solute-freezing phenomena, modeling is an ideal approach for quantifying these relationships. However, quantifying aqueous-solute properties at subzero temperatures poses many experimental difficulties. As a consequence, our ability to model these systems is frequently limited by lack of basic data. The models reviewed in this section, however, do indicate that significant progress has been made in the past decade, which bodes well for the future.

RECOMMENDATIONS

Much research in cold regions is ultimately prompted by a quest for solving practical problems. Five major problems of cold regions associated with freezing and thawing are soil strength, frost heaving, revegetation of severely disturbed lands, global carbon balance and contaminant transport. This review has identified several important aspects of chemistry and freezing–thawing processes that impact on these problems.

- Chemical thermodynamic equilibria of aqueous electrolyte solutions at subzero temperatures are poorly understood. This is especially true of the solubilities of Ca, Mg, K and Na sulfates, bicarbonates and carbonates, important salts in many saline soils and seawater. Chemical activities and mineral solubilities play a fundamental role in controlling the chemical potential of water and ice in soils, the freezing-point depression and the unfrozen water content, which, in turn, play important roles in controlling the fluxes of water and solutes in soils.

- There are strong and complex interactions among soil properties that control solute and water flows along concentration, temperature and hydrostatic gradients in freezing and frozen soils. These complex interactions *necessitate* the development of computer simulation models that can integrate physical and chemical properties and processes. The ultimate goal is to develop models that can accurately address practical problems such as soil strength, frost heaving and contaminant transport in freezing and frozen soils.

- Does the freeze–thaw process significantly alter soil gas (O_2, CO_2, N_2O, CH_4) concentrations? This has important ramifications for carbon and nitrogen balance; nutrient availability; microbial, enzymatic and plant activity; soil

oxidation–reduction status; and mineral solubility.

- Microbial activity exists to temperatures as low as –10°C. The ability of microbes to decompose contaminants or plants to absorb contaminants (immobilization) is poorly understood for low temperatures. Recent work suggests that the winter "dormant" season may be a misnomer in describing microbial activity and carbon balance. Microbes and plants adapted to cold regions have been subjected to different selective pressures during evolution and may not respond the same as their better-studied temperate counterparts.
- What are optimal conditions for solute exclusion in freezing soils? This has important implications for decontaminating soils.

To further our understanding of chemistry and freeze–thaw processes in soils, future work should be directed along these lines, with major foci on both simulation modeling and empirical studies.

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This review broadly examines the interactions between freeze–thaw processes and soil chemistry, focusing on 1) the effect of solutes on physical properties such as freezing-point depression, unfrozen water and frost heaving, 2) the effect of freeze–thaw cycles and low temperatures on soil chemistry, and 3) modeling of freeze–thaw processes and chemistry. The presence of solutes causes a freezing-point depression, which increases the amount of unfrozen water in soils. Liquid films on soil particles provide the dominant route for the flow of water and associated solutes in frozen soils. In general, salts reduce the hydraulic conductivity and water flow to the freezing front, which reduces frost heaving. Solute exclusion during freezing leads to supersaturated solutions, which promotes the precipitation of secondary minerals in soils. At the watershed level, ionic concentrations in early meltwaters are often 2–9 times higher than snowpack concentrations. Temperature is the dominant factor controlling decomposition rates, with minimal detectable rates occurring at temperatures as low as $-10°C$; both bacteria and fungi are physiologically active at subzero temperatures. Extracellular enzymes are active in soils at temperatures as low as $-20°C$; this activity is thought to occur in unfrozen water on surfaces of soil particles. Nitrogen mineralization is reported at temperatures as low as $1°C$ and is promoted by freeze–thaw cycles. There are strong and complex interactions among soil properties that control solute and water flows along concentration, temperature and hydrostatic gradients in freezing and frozen soils. These complex interactions *necessitate* the development of computer simulation models that can integrate physical–chemical properties and processes.

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